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Cyclopentadiene with two coordinating sites: 1,5-bis(diphenylphosphino)-2,3,4-trimethylcyclopenta-1,3-diene

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Abstract

The possibility of obtaining the new hidentate 1,2-diphenylphosphinocyclopentadienyl ligand has been studied. 1,5-bis(diphenylphosphino)-2,3,4-trimethylcyclopenta-1,3-diene can be formed from butanone and chlorodiphenylphosphine in eight steps. The results of chemical and spectroscopic studies reveal that a 1,5-sigmatropic migration of the diphenylphosphino group takes place: the 1,2-diphenylphosphino-substituted species are converted into 1,3 species.

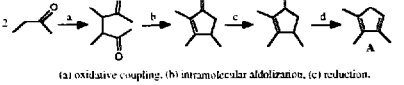
Keywords: Phosphine; Cyclopentadiene; Chalcogen; Diphosphine; Group 6

1. Introduction

The synthesis of multidentate ligands combining a cyclopentadienyl ligand with chelating substituents (such as phosphino groups) is one of our centres of interest in the organometallic chemistry field [1]. Our researches concerning the access to new edifices of this family have made us develop new methods for the synthesis of substituted cyclopentadienyl salts: mono or bis(diphenylphosphino)trimethylcyclopentadienyl. Blocking three adjacent positions of a cyclopentadienyl skeleton and then introducing the phosphino groups in vicinal positions, was our initial aim. We report here the spectroscopic analysis of the phosphinocyclopentadienes obtained from 1,2,3-trimethylcyclopentadiene salts, as well as an study of their reactivity.

2. Results and discussion

1,2,3-Trimethylcyclopenta-1,3-diene is prepared by modifying the experimental procedure that has already been described briefly [2] (Eq. (1)). In our hands, the overall yield is about 25%, whereas it was given as only about 9% in Ref. [2].

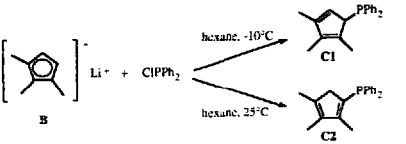


(a) oxidative coupling, (b) intramolecular aldolization, (c) reduction, (d) dehydration and rearrangement

(1)

The aromatization of **A** is performed by the action of methyllithium in diethyl ether, leading to a solid **B**, which is stable under argon.

The cyclopentadienyl and tetramethylcyclopentadienyl anions react toward chlorodiphenylphosphine to give the corresponding neutral and monophosphorated species [3]. The transposition of this reaction to the 1,2,3-trimethylcyclopentadienyl anion could lead to a complex mixture. Five isomers can a priori be formed. In fact, a regiospecific reaction takes place and only one isomer is formed. The nature of this isomer is highly dependent on the temperature conditions used (Eq. (2)).



(2)

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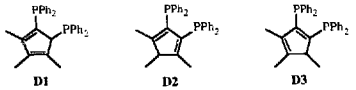
The reaction is performed in hexane, and a quantity of chlorophosphine lower than the stoichiometry required is used (in order to prevent any pollution of the product by this reagent, which is difficult to eliminate). The phosphines **C1** and **C2** are hexane soluble and can be separated from the excess of the lithium salt **B** and from the lithium chloride by simple filtration of the mixture.

C1 and **C2** are white solids, stable under inert atmosphere. The species **C1** is unstable in solution and is transformed totally into **C2** via a 1,5-sigmatropic transposition. This evolution is slow enough to enable ^{1}H and ^{31}P NMR studies, but it has not been possible to obtain the ^{13}C NMR spectrum from the solution of **C1** without observing the appearance of **C2**.

The nature of each product was determined unambiguously by NMR spectra analysis. **C1** is the only isomer to possess both a hydrogen atom with a $^{2}J(P–H)$ coupling constant and a hydrogen atom with a $^{3}J(P–H)$ coupling constant; by contrast, a methylenic group exists only in the isomer **C2**. Moreover, the chemical shifts are very different for each case: 3.94 ppm and 5.79 ppm respectively for the hydrogen atoms in a and b positions to the phosphorus atom of **C1**, and 2.67 ppm for the methylenic protons of **C2**. The difference observed in ^{31}P NMR (−4.6 ppm for **C1** and −2/.2 ppm for **C2**) confirms that the phosphorus atom is bonded to an sp^3 carbon atom in **C1** and to an sp^2 carbon atom in **C2**.

The cyclopentadienes **C1** and **C2** are easily aromatizable. The action of one more equivalent of chlorodiphenylphosphine on their lithium salt leads to an original penta-substituted cyclopentadiene, possessing two phosphorus atoms bonded to two adjacent carbon atoms. At first sight, three isomers could be formed:

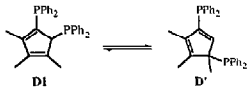


As for the fixation of the first phosphorus atom leading to **C1** and **C2**, the reaction is performed in hexane and with a default of chlorodiphenylphosphine. Whatever the temperature of the reaction, the same major compound is always isolated. It corresponds to the 1,2-diphosphorylated isomer **D1**, the structure of which is unambiguously determined by NMR spectroscopy.

The diphenylphosphino groups in **D1** are effectively in positions very different from those occupied in **D2** and **D3**. In ^{31}P NMR, two doublets ($^{3}J(P–P) = 54$ Hz) are observed at −1.5 ppm and −20.5 ppm, corresponding respectively to one phosphorus atom bonded to the sp^3 carbon atom and to the other one bonded to the ethylene carbon atom. In ^{1}H NMR, it is worth noting that the signal corresponding to the only hydrogen atom supported by a carbon atom of the ring appears as a large singlet at 3.95 ppm.

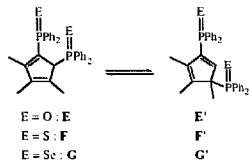
The formation of the only isomer **D1**, and the absence of evolution to the isomers **D2** or **D3**, differs from what is observed for the trimethyldiphenylphosphinocyclopentadienes **C**. **D1** must be the kinetic product, resulting from the addition on the less sterically hindered carbon atom of the cyclopentadienyl ring, and probably for steric reasons, **D1** does not evolute into **D2** or **D3**.

The diphosphine **D1** is not the only species to be formed in the reaction mixture. The ^{1}H and ^{31}P NMR spectra of a solution of **D1** reveal the presence of a small amount of a second diphosphine (7%) which cannot be identified as a **D**-type isomer. This minor species must be the 1,3-diphosphine **D'**, the formation of which is the result of a 1,5-sigmatropic transposition from **D1** (Eq. (3)).



(3)

This interpretation is reinforced by the study of the reactivity of **D1** toward oxygen, sulphur and selenium. The transformation P(III) → P=E (P(V); E = O, S, Se) (Eq. (4)) occurs simultaneously to the evolution of the relative proportions of the 1,2- and 1,3-diphosphines species. Table 1 shows the increasing proportion of the 1,3-species, following the sequence **D**, **E**, **F**, **G** (free-, oxidized-, sulphurized- and seleniated-phosphine respectively). The importance of the steric hindrance on the relative stability of the 1,2- and 1,3-species is certainly responsible for this evolution.



(4)

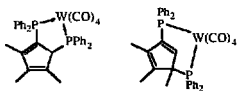
The 1,2 ⇔ 1,3 exchange rate is slow enough, at the NMR time scale, to enable the observation of each diphosphine spectrum. These spectra are not modified when the temperature increases from 25 °C to 80 °C. In ^{1}H NMR, a systematic evolution of the chemical shifts

Table 1
1,2- and 1,3-diphosphines relative proportions (observed in ^1H and ^{31}P NMR)

	Diphosphine (%)	
	1,2	1,3
D	93	7
E	64	36
F	20	80
G	10	90

is observed according to the sequence: oxidized, sulphurized, and seleniated species. In ^{31}P NMR, the evolution is the same as that observed for the Ph_3P=E-type species ($\Delta\delta > 0$ when E turns from oxygen to sulphur, and $\Delta\delta < 0$ when it turns from sulphur to selenium) [4]. The signal of the phosphorus atom bonded to the sp^3 carbon atom of the cyclopentadienyl ring in **D'** is deshielded about 17.5 ppm compared with **D1**. A similar deshielding is also observed if the phosphorus chemical shifts of $P(^iPr)_3$ (19 ppm) and $P(^tBu)_3$ (73 ppm) are compared [4].

We have tried to trap and stabilize both diphosphines by making them react with the $W(CO)_4$ fragment, coming from the thermal dissociation of $W(CO)_4(pip)_2$ (pip = piperidine) [5]. Two products, **H1** (70%) and **H2** (30%), were effectively formed and easily differentiated by ^1H and ^{31}P NMR. On the basis of the NMR data, the structures given below were postulated. However, the infrared spectrum does not exhibit the two sets of absorption bands normally expected for such a mixture, and the separation of these isomers by recrystallization or chromatography has so far been unsuccessful.



H1 70 % **H2** 30 %

3. Conclusion

We have performed a chemical pathway leading to new diphosphines, bis(diphenylphosphino)trimethylcyclopentadienes. The complexity of the mixture obtained is not an obstacle to its use in organometallic chemistry because the aromatization and the formation of the lithium salt are possible only for the 1,2-diphosphine. The utilization of such a salt for the preparation of metallocenes is being studied.

4. Experimental section

Reactions were carried out under an atmosphere of argon by means of conventional Schlenk techniques. Solvents were dried and deoxygenated before distillation from sodium benzophenone ketyl or Na–K alloy. Ph_2PCl was distilled under argon before utilization. Elemental analyses were performed by the Service Central d'Analyses du CNRS. Mass spectra (electronic ionization 70 eV) were recorded on a Kratos concept IS machine. ^1H, ^{31}P and ^{13}C NMR spectra were recorded on a Bruker AC 200. The spectra were referenced to TMS or H_3PO_4. ^{13}C spectra were recorded using the JMOD technique. The following abbreviations appear in the text: I, II, III and IV for the primary, secondary, tertiary and quaternary carbon atoms respectively.

4.1. Meso and racemic 3,4-dimethylhexane-2,5-dione [6]

A suspension of PbO_2 (300 g; 1.25 mol) in butanone (800 ml) was heated to reflux for 9 h. The orange suspension was then cooled, filtered and the orange solid was washed three times with 100 ml portions of butanone. The yellow-orange filtrate and the various layers were collected and dried over anhydrous $MgSO_4$. The butanone was reprocessed by distillation (10 mm Hg, room temperature). Vacuum distillation (7 mm Hg, 50–80 °C) of the brown oily residue thus obtained gave a mixture of the two expected diastereoisomers (70 g; 0.49 mmol; 40% yield).

4.1.1. Racemic γ-diketone

^1H NMR, C_6D_6: 0.66 (pd, 3H, Me [β CO], ^3J(H–H) = 6.6 Hz); 1.83 (s, 3H, Me [α CO]); 2.55 (m, 1H, CH). ^{13}C NMR, $CDCl_3$: (I) 13.3 (Me [β CO]); 28.3 (Me [α CO]); (III) 48.1 (CH); (IV) 211.5 (CO).

4.1.2. Meso γ-diketone

^1H NMR, C_6D_6: 0.81 (pd, 3H, Me [β CO], ^3J(H–H) = 6.6 Hz); 1.70 (s, 3H, Me [α CO]); 2.50 (m, 1H, CH). ^{13}C NMR, $CDCl_3$: (I) 14.4 (Me [β CO]); 28.8 (Me [α CO]); (III) 48.5 (CH); (IV) 210.4 (CO).

4.2. Trimethylcyclopent-2-enones

The mixture of the γ-diketones (35.5 g; 250 mmol) was added to 300 ml of a boiling aqueous sodium hydroxide solution (2.5 g; 62.5 mmol) and then the reflux was maintained for 15 min. The mixture was then rapidly cooled and extracted with diethyl ether. The organic layers were collected, washed with distilled water and dried over anhydrous $MgSO_4$. The solvent was removed and the yellow oily residue was distilled under 5 mm Hg. The core fraction (24.06 g; 194 mmol;

78% yield) was distilled at 61–64 °C and contained a mixture of 2,3,4-trimethylcyclopent-2-enone (80%) and 3,4,5-trimethylcyclopent-2-enone (20%).

4.2.1. 3,4,5-Trimethylcyclopent-2-enone

^{1}H NMR, C_6D_6: 0.65 (d, 3H, Me [β CO], ^3J(H–H) = 7.0 Hz); 1.06 (d, 3H, Me [α CO], ^3J(H–H) = 7.4 Hz); 1.39 (s, 3H, Me [β CO]); 1.65 (m, 1H, H [β CO]); 2.02 (m, 1H, H [α CO]); 5.73 (s, 1H, ethylene H).

4.2.2. 2,3,4-Trimethylcyclopent-2-enone

^{1}H NMR, C_6D_6: 0.64 (d, 3H, Me [β CO], ^3J(H–H) = 7.1 Hz); 1.37 (s, 3H, Me [β CO]); 1.60 (m, 3H, Me [α CO]); 1.74 (m, 1H, H [β CO]); 2.24 (d, 1H, H [α CO], ^3J(H–H) = 6.8 Hz); 2.33 (d, 1H, H [α CO], ^3J(H–H) = 6.6 Hz). ^{13}C NMR, $CDCl_3$: (I) 7.6 (Me); 14.4 (Me); 18.7 (Me); (II) 41.8 (CH_2); (III) 36.9 (CHMe); (IV) 135.9 (ethylene C); 172.8 (ethylene C); 207.1 (CO).

4.3. Trimethylcyclopentenols

To a grey suspension of $AlLiH_4$ (9.85 g; 25.9 mmol) in diethyl ether (300 ml) previously cooled to 0 °C was added dropwise a solution of the cyclopentenones (32.14 g; 25.9 mmol) in diethyl ether (60 ml). The mixture was allowed to warm to room temperature and then stirred for 12 h. It was then very slowly hydrolysed with water-saturated diethyl ether until a white precipitate appeared. The organic layers collected were washed with water, dried over $MgSO_4$ and filtered. The solvent was then removed leading to a yellow-green oil (29.25 g; 23.2 mmol; 90% yield) containing a mixture of 3,4,5-trimethylcyclopent-2-en-1-ol and 2,3,4-trimethylcyclopent-2-en-1-ol in the same proportions as the initial cyclopentenones.

4.3.1. 2,3,4-Trimethylcyclopent-2-en-1-ol

^{1}H NMR, C_6D_6: 0.96 (d, 3H, Me [β COH], ^3J(H–H) = 6.8 Hz); 1.45 (m, 3H, Me [β COH]); 1.59 (m, 3H, Me [α COH]); 2.10–2.40 (m, 2H); 1.05–1.16 (m, 1H); 2.25–2.35 (m, 1H); 4.30 (ps, 1H, OH). ^{13}C NMR, $CDCl_3$: (I) 11.3 (Me); 12.1 (Me); 20.4 (Me); (II) 41.8 (CH_2); (III) 41.2 (CHMe); 79.4 (CHOH); (IV) 133.5 (ethylene C); 138.8 (ethylene C).

4.3.2. 3,4,5-Trimethylcyclopent-2-en-1-ol (partial attribution)

0.83 (d, 3H); 1.01 (d, 3H); 1.48 (m, 3H) for three methyl groups.

4.4. 1,2,3-Trimethylcyclopenta-1,3-diene

A solution of the mixture of the trimethylcyclopentenols (29.25 g; 235 mmol) in diethyl ether (200 ml) was slowly (3 h) added at room temperature to a mixture of diethyl ether (200 ml) and hydrochloric acid (three-times diluted, 3 ml). The stirring was maintained until two layers appeared (6 h). The mixture was allowed to settle and the aqueous layer was eliminated. The organic layer was washed with an aqueous saturated sodium chloride solution and dried over $MgSO_4$. After filtration and removal of the solvent (without heating), 22.84 g (211 mmol; 90% yield) of a colourless liquid **A** were obtained. **A** did not need further distillation and was used directly in the following hours.

^{1}H NMR, $CDCl_3$: 1.79 (s, 3H, Me); 1.90 (m, 6H, Me); 2.75 (m, 2H, CH_2); 5.81 (s, 1H, ethylene H).

4.5. 1,2,3-Trimethylcyclopentadienyllithium anion B

To a solution of 1,2,3-trimethylcyclopenta-1,3-diene **A** (9.33 g; 86.3 mmol) in diethyl ether (80 ml) previously cooled to 0 °C were added dropwise 70 ml of an ethereal solution of methyllithium (c = 1.35 mol l^{-1}). A gaseous emission and a white fluffy precipitate were observed. At the end of the addition, the mixture was stirred at room temperature overnight. It was then filtered and the precipitate was washed with diethyl ether (3 × 30 ml). Removing the solvent led to a white solid **B** (8.8 g; 77.2 mmol; 89% yield) which can be stored for some time under argon.

^{1}H NMR, THF-d_8: 1.80 (s, 3H, Me); 1.86 (m, 6H, Me); 4.96 (m, 2H). ^{13}C NMR, THF-d_8: (I) 15.3 (1C, Me); 17.4 (2C, Me); (III) 101.3 (2C, C–H); (IV) 111.4 (1C, C–Me); 112.7 (2C, C–Me).

4.6. 1-Diphenylphosphino-2,3,4-trimethylcyclopenta-1,3-diene C2

To a suspension of 1,2,3-trimethylcyclopentadienyllithium **B** (3.96 g; 34.7 mmol) in hexane (75 ml) was added dropwise and at room temperature a solution of chlorodiphenylphosphine (7.28 g; 33 mmol) in diethyl ether (50 ml). After 2 h under stirring, the mixture was filtered and the precipitate was washed three times with 25 ml of hexane. The yellow filtrate and the colourless layers were collected and the solvent was removed, leading to a colourless thick oil. After addition of 10 ml of cold pentane, a fluffy white solid (9.1 g; 31 mmol; 94% yield) was obtained. It was then washed with pentane (3 × 10 ml) and dried under vacuo.

Note: the chlorophosphine Ph_2PCl must be used in quantities lower than needed because, at the end, it is collected with the filtrate and it cannot be separated from the product.

Anal. Found: C, 81.49; H, 7.17; P, 10.47. $C_{20}H_{21}P$. Calc.: C, 82.15; H, 7.24; P, 10.60%. Mass spectrum (EI): 292 [M^+, 100]; 277 [$(M-CH_3)^+$, 5]; 215 [$(M-Ph)^+$, 15]; 185 [$(PPh_2)^+$, 35]. ^{1}H NMR, $CDCl_3$: 1.86 (m, 3H, Me); 1.89 (s, 3H, Me); 2.16 (s, 3H, Me); 2.67 (s, 2H, CH_2); 7.30–7.34 (m, 10H, phenyl). ^{13}C NMR,

$CDCl_3$: (I) 11.2 (s, Me); 13.9 (s, Me); 14.3 (s, Me); (II) 47.1 (d, CH_2, ^2J(P–C) = 4.2 Hz); (III) 128.1 (s, para); 128.4 (d, meta, ^3J(P–C) = 6.3 Hz); 133.1 (d, ortho, ^2J(P–C) = 18.5 Hz); (IV) 128.8 (d, ipso Cp, ^1J(P–C) = 7.2 Hz); 137.0 (d, Cp, J(P–C) = 6.8 Hz); 139.4 (d, Cp, J(P–C) = 8.2 Hz); 142.0 (s, Cp); 156.6 (d, ipso phenyl, ^1J(P–C) = 31.7 Hz). ^{31}P NMR, $CDCl_3$: −27.2 (s).

Note: the other isomer (**C1**) has been obtained selectively, using the same quantities of reagents and solvent, but proceeding at −10 °C (reaction and evaporation). After removal of the solvent, a white solid identified as the 5-diphenylphosphino-1,2,3-trimethylcyclopenta-1,3-diene **C1** was obtained.

^{1}H NMR, $CDCl_3$: 1.72 (m, 6H, Me); 1.80 (pq, 3H, Me, J = 1.8 Hz); 3.94 (broad s, 1H, CHP); 5.79 (broad s, 1H, ethylene H); 7.27–7.49 (m, 6H, phenyl); 7.60–7.65 (m, 4H, phenyl). ^{13}C NMR, $CDCl_3$: (I) 10.9 (s, Me); 13.8 (s, Me); 14.1 (s, Me); (III) 52.4 (d, ipso Cp, ^1J(P–C) = 19.6 Hz); 125.5 (broad s, Cp); 127.7 (s, para); 127.8 (s, para'); 128.3 (d, meta, ^3J(P–C) = 6.4 Hz); 128.7 (d, meta', ^3J(P–C) = 7.4 Hz); 133.1 (d, ortho, ^2J(P–C) = 12.2 Hz); 133.5 (d, ortho', ^2J(P–C) = 12.9 Hz); (IV) 137.6 (d, Cp, J(P–C) = 8.8 Hz); 138.5 (d, Cp, J(P–C) = 18.1 Hz); 144.7 (d, Cp, J(P–C) = 3.7 Hz); 156.5 (d, ipso phenyl, ^1J(P–C) = 32.2 Hz); 175.5 (d, ipso' phenyl, ^1J(P–C) = 35.3 Hz). ^{31}P NMR, $CDCl_3$: −4.6 (s).

4.7. 1-Diphenylphosphino-2,3,4-trimethylcyclopentadienyllithium anion

To a white suspension of 1-diphenylphosphino-2,3,4-trimethylcyclopenta-1,3-diene **C2** (6.0 g; 20.5 mmol) in hexane (75 ml) previously cooled to 0 °C, were added dropwise 9.4 ml (22.6 mmol) of a solution of butyllithium in hexane (c = 2.4 mol l^{-1}). The mixture turned from white to yellow and was stirred overnight. The cream-white solid thus obtained was filtered and washed three times with 30 ml of hexane. After removal of the solvent, 5.22 g (17.5 mmol; 85% yield) of a very air-sensitive solid were obtained.

^{1}H NMR, THF-d_8: 1.98 (s, 3H, Me); 1.99 (s, 3H, Me); 2.08 (s, 3H, Me); 5.27 (d, 1H, Cp, ^3J(P–H) = 2.5 Hz); 7.07–7.17 (m, 6H, phenyl); 7.24–7.33 (m, 4H, phenyl). ^{1}H NMR, C_6D_6: 1.42 (s, 3H, Me); 1.80 (s, 3H, Me); 2.13 (s, 3H, Me); 5.16 (s, 1H, Cp); 7.16 (ps, 6H, phenyl); 7.47 (ps, 4H, phenyl). ^{31}P NMR, THF-d_8: −18.0 (s). ^{31}P NMR, C_6D_6: −28.3 (s).

4.8. 1,5-Bis(diphenylphosphino)-2,3,4-trimethylcyclopenta-1,3-diene

To a suspension of 1-diphenylphosphino-2,3,4-trimethylcyclopentadienyllithium (4.54 g; 15.2 mmol) in hexane (90 ml) was added dropwise and at −80 °C a solution of chlorodiphenylphosphine (3.0 g; 13.7 mmol) in hexane (30 ml). At the end of the addition, the mixture was allowed to warm to room temperature and then stirred for 2 h. It was then filtered and extracted twice with 30 ml of hexane. The white solid (LiCl) was eliminated and the solvent was removed. The yellow product (5.44 g; 11.4 mmol; 83% yield) thus obtained was recrystallized in the minimum of pentane, affording white thin crystals. NMR analysis indicated 93% of the material was **D1** and 7% was **D'**.

Anal. Found: C, 80.35; H, 6.63; P, 12.05. $C_{32}H_{30}P_2$. Calc.: C, 80.66; H, 6.35; P, 13.00%. Mass spectrum (EI): 476 [M^+, 65]; 399 [$(M - Ph)^+$, 60]; 367 [$(M - PPh - H)^+$, 60]; 291 [$(M - PPh_2)^+$, 85]; 275 [$(M - PPh_2 - Me - H)^+$, 45]; 262 [$(M - PPh_2 - 2Me - H)^+$, 100]; 215 [$(M - PPh_2 - Ph)^+$, 80].

D1; ^{1}H NMR, $CDCl_3$: 1.45–1.48 (m, 6H, Me); 1.60 (s, 3H, Me); 3.95 (ps, 1H, CHP); 7.19–7.42 (m, 20H, phenyl). ^{31}P NMR, $CDCl_3$: −1.5 (d, P–C(sp^3), ^3J(P–P) = 54.0 Hz); −20.5 (d, P–C(sp^2), ^3J(P–P) = 54.0 Hz). ^{13}C NMR, $CDCl_3$: (I) 11.4 (poor resolved pt, Me); 15.0 (poor resolved pt, Me); 15.5 (poor resolved pt, Me); (III) 60.5 (dd, ipso Cp, ^1J(P–C) = 45.1 Hz, ^2J(P–C) = 15.5 Hz); 127.8–129.8 (7 singlets of various intensity); 132.3 (d, ortho, ^2J(P–C) = 16.3 Hz); 133.9 (d, ortho, ^2J(P–C) = 19.5 Hz); 134.2 (d, ortho, ^2J(P–C) = 19.1 Hz); 135.3 (d, ortho, ^2J(P–C) = 22.0 Hz); (IV) 130.1 (d, ipso Cp, ^1J(P–C) = 8.5 Hz); 133.6 (d, Cp, J(P–C) = 20.0 Hz); 138.2 (d, Cp, J(P–C) = 11.0 Hz); 138.6 (dd, ipso phenyl, ^1J(P–C) = 5.1 Hz, ^4J(P–C) = 2.3 Hz); 138.8 (d, Cp, J(P–C) = 2.1 Hz); 138.9 (dd, ipso phenyl, ^1J(P–C) = 3.9 Hz, ^4J(P–C) = 1.4 Hz); 143.9 (dd, ipso phenyl, ^1J(P–C) = 3.9 Hz, ^4J(P–C) = 2.3 Hz); 153.1 (dd, ipso phenyl, ^1J(P–C) = 9.9 Hz, ^4J(P–C) = 8.0 Hz).

D': ^{1}H NMR, $CDCl_3$: 1.18 (d, 3H, Me, ^3J(P–H) = 14.3 Hz); 1.68 (s, 3H, Me); 2.00 (s, 3H, Me); 5.89 (d, 1H, ethylene H, ^3J(P–H) = 3.0 Hz); 6.95–7.42 (m, 20H, phenyl). ^{31}P NMR, $CDCl_3$: −21.5 (broad s); +16.2 (broad s).

4.9. Phosphine dioxides E

To a solution of 0.3 g (0.63 mmol) of the diphosphines **D** in toluene (10 ml) were added dropwise and at room temperature 2 ml of a 25% hydrogen peroxide solution. The heterogeneous mixture was stirred for 15 min and then left to settle. The organic layer was extracted and dried over $CaCl_2$. After removal of the toluene, 0.31 g (0.61 mmol; 97% yield) of a white solid was isolated. The NMR analysis indicated 64% of the material was the dioxide **E** and 36% was its isomer **E'**.

E; ^{1}H NMR, $CDCl_3$: 1.45 (s, 3H, Me); 1.47 (broad s, 3H, Me); 1.90 (s, 3H, Me); 4.93 (dd, 1H, CHP, ^1J(P–H) = 24.0 Hz, ^3J(P–H) = 1.5 Hz); 7.15–7.25 (m, 20H, phenyl). ^{31}P NMR, $CDCl_3$: 18.7 (s); 33.1 (s). ^{13}C NMR, $CDCl_3$ (partial attribution): (III) 63.5 (dd, ipso sp^3 Cp, ^1J(P–C) = 50.2 Hz, ^2J(P–C) = 12.5 Hz).

E'; ^{1}H NMR, $CDCl_3$: 1.39 (d, 3H, Me, ^3J(P–H) = 11.7 Hz); 1.67 (broad s, 3H, Me); 1.96 (s, 3H, Me); 6.40 (d, 1H, ethylene H, ^3J(P–H) = 12.0 Hz); 7.20–7.80 (m, 20H, phenyl). ^{31}P NMR, $CDCl_3$: 22,6 (s); 33.5 (s). ^{13}C NMR, $CDCl_3$ (partial attribution): (IV) 63.5 (dd, ipso sp^3 Cp, ^1J(P–C) = 55.5 Hz, ^3J(P–C) = 14.0 Hz).

4.10. Phosphino disulphides F

To a suspension of an excess of sulphur (0.05 g; 1.56 mmol) in toluene (10 ml), was added dropwise and at room temperature a solution containing 0.23 g (0.48 mmol) of the mixture of the diphosphines **D**. After 8 h under stirring, the excess of sulphur was eliminated by filtration and the solvent was removed, leading to a white powder (0.21 g; 0.39 mmol; 81% yield). NMR analysis showed a mixture composed of the disulphur isomers **F'** (80%) and **F** (20%).

Mass spectrum (EI) of the mixture: 540 [M$^+$, 70]; 323 [(M – PPh_2S)$^+$, 90]; 291 [(M – PPh_2S – S)$^+$, 10]; 217 [(PPh_2S)$^+$, 100].

F; ^{1}H NMR, $CDCl_3$: 1.41 (broad s, 3H, Me); 1.43 (broad s, 3H, Me); 1.71–1.75 (m, 3H, Me); 5.90 (s, 1H, CHP); 6.80–8.20 (m, 20H, phenyl). ^{31}P NMR, $CDCl_3$: 33.3 (s); 49.3 (s). ^{13}C NMR, $CDCl_3$ (partial attribution): (III) 62.4 (dd, ipso sp^3 Cp, ^1J(P–C) = 34.5 Hz, ^2J(P–C) = 14.7 Hz).

F'; ^{1}H NMR, $CDCl_3$: 1.50 (d, 3H, Me, ^3J(P–H) = 18.2 Hz); 1.65 (d, 3H, Me, ^4J(P–H) = 2.7 Hz); 1.78 (s, 3H, Me); 5.98 (dd, 1H, ethylene H, ^3J(P–H) = 10.0 Hz, ^3J(P–H) = 2.2 Hz); 6.80–8.30 (m, 20H, phenyl). ^{31}P NMR, $CDCl_3$: 33.1 (s); 51.4 (s). ^{13}C NMR, $CDCl_3$ (partial attribution): (IV) 62.1 (dd, ipso sp^3 Cp, $^1J_{PC}$ = 34.5 Hz, ^2J(P–C) = 14.7 Hz).

4.11. Phosphino diselenides G

The experimental procedure was similar to that used for the preparation of the disulphurs **F** and **F'**, replacing sulphur by grey selenium powder and maintaining the stirring for 12 h. A white solid containing compounds **G'** (90%) and **G** (10%) was thus obtained.

Mass spectrum (EI) of the mixture: 636 [M$^+$, 10]; 372 [(M – PPh_2Se)$^+$, 60]; 291 [(M – PPh_2Se – Se)$^+$, 20]; 265 [(PPh_2Se)$^+$, 65]; 215 [(M – PPh_2Se – Ph – Se)$^+$, 30].

G; ^{1}H NMR, $CDCl_3$: 1.37 (broad s, 3H, Me); 1.44 (m, 3H, Me); 1.79 (broad s, 3H, Me); 6.30 (d, 1H, CHP, ^2J(P–H) = 17.8 Hz); 6.71–8.33 (m, 20H, phenyl). ^{31}P NMR, $CDCl_3$: 24.4 (s); 50.7 (s).

G'; ^{1}H NMR, $CDCl_3$: 1.55 (d, 3H, Me, J(P–H) = 20.0 Hz); 1.68 (d, 3H, Me, J(P–H) = 2.0 Hz); 1.77 (s, 3H, Me); 5.93 (dd, 1H, ethylene H, ^3J(P–H) = 10.0 Hz, ^3J(P–H) = 2.4 Hz); 7.25–7.95 (m, 20H, phenyl). ^{31}P NMR, $CDCl_3$: 22.4 (s); 46.2 (s).

4.12. Tungstacarbonyl complexes H

A solution of 1.07 g (2.24 mmol) of the mixture **D1** + **D'** in THF (30 ml) was added to a suspension of $W(CO)_4(pip)_2$ (1.16 g; 2.49 mmol) in THF (10 ml). The heterogeneous mixture was heated to reflux for 90 min, after which time it had turned to a brown solution. After removal of the solvent and several washes with pentane, a yellow solid (1.66 g; 2.15 mmol; 96% yield) containing a mixture of complexes **H1** (70%) and **H2** (30%) was obtained.

Mass spectrum (EI) of the mixture: 772 [M$^+$, 20]; 688 [(M – 3CO)$^+$, 15]; 660 [(M – 4CO)$^+$, 30]; 476 [(M – $W(CO)_4$)$^+$, 30]; 367 [(M – $W(CO)_4$ – PPh_2 – H)$^+$, 10]. IR, THF (νCO, cm^{-1}) of the mixture: 1881; 1897; 1914; 2015.

H1; ^{1}H NMR, $CDCl_3$: 1.29 (s, 3H, Me); 1.51 (s, 3H, Me); 1.82 (s, 3H, Me); 3.18 (pd, 1H, CHP, ^2J(P–H) = 7.6 Hz); 6.94–7.78 (m, 20H, phenyl). ^{31}P NMR, $CDCl_3$: 10.9 (d, ^3J(P–P) = 7.7 Hz); 20.8 (d, ^3J(P–P) = 7.7 Hz); $^1J(^{31}P^{183}W)$ = 217 Hz.

H2; ^{1}H NMR. $CDCl_3$: 0.83 (d, 3H, Me, ^3J(P–H) = 8.0 Hz); 1.45 (broad s, 3H, Me); 1.86 (s, 3H, Me); 4.03 (dq, 1H, CHP, ^3J(P–H) = 18.8 Hz, ^3J(P–H) = 1.5 Hz); 6.94–7.79 (m, 20H, phenyl). ^{31}P NMR, $CDCl_3$: 24.6 (s); 28.1 (s); $^1J(^{31}P^{183}W)$ = 217 Hz.

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References

[1] S. Ninoreille, R. Broussier, R. Amardeil, M.M. Kubicki and B. Gautheron, *Bull. Soc. Chim. Fr., 132* (1995) 128.
[2] J.R. Sowa and R.J. Angelici, *J. Am. Chem. Soc., 113* (1991) 2537.
[3] (a) J. Szymoniak, J. Besançon, A. Dormond and C. Moïse, J. Org. Chem., 55 (1990) 1429. (b) F. Mathey and J.P Lampin, *J. Organomet. Chem., 31* (1975) 2685.
[4] (a) W. McFarlane and D.S. Rycroft, *J. Chem. Soc. Dalton Trans.*, (1973) 2162. (b) J. Mason, *Multinuclear NMR*, Plenum Press, 1989.
[5] D.J. Darensbourg and R.L. Kump, *Inorg. Chem., 17* (1978) 2680.
[6] G. Szakàl-Quin, D.G. Graham, D.S. Millington, D.A. Maltby and A.T. McPhail, *J. Org. Chem., 51* (1986) 621.